

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-042813

(43)Date of publication of application : 08.02.2002

(51)Int.Cl.

H01M 4/58
C01G 53/00
H01M 4/02
H01M 10/40

(21)Application number : 2000-227858

(71)Applicant : MATSUSHITA ELECTRIC IND CO
LTD

(22)Date of filing : 27.07.2000

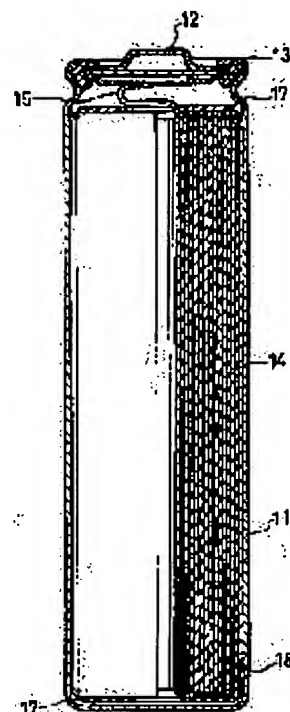
(72)Inventor : KOTSUKI TSUTOMU
YOSHIZAWA KOJI
NAGAYAMA MASATOSHI

(54) POSITIVE ELECTRODE ACTIVE MATERIAL AND NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a low-cost and high-capacity non-aqueous electrolyte battery.

SOLUTION: The non-aqueous electrolyte secondary battery comprises a negative electrode mainly using a material capable of storing and releasing at least lithium ions or metallic lithium, as a negative electrode active material, a separator, a positive electrode and an electrolyte. An active material for the positive electrode is oxide containing nickel and manganese elements, and the percentage contents of the nickel and manganese elements are substantially the same.



LEGAL STATUS

[Date of request for examination] 17.12.2004

[Date of sending the examiner's decision of
rejection] 29.06.2006

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number] 3890185

[Date of registration] 08.12.2006

[Number of appeal against examiner's decision of
rejection] 2006-016467

[Date of requesting appeal against examiner's
decision of rejection] 31.07.2006

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] Positive active material for nonaqueous electrolyte cells whose crystal structure of said crystal grain child it consists of a crystal grain child of the oxide which contains the nickel element and manganese element of this ratio substantially, and is rhombohedron structure.

[Claim 2] Positive active material for nonaqueous electrolyte cells according to claim 1 whose die length of the c-axis which belonged as hexagonal system in said crystal grain child's crystal structure is 14.25Å or more.

[Claim 3] Positive active material for nonaqueous electrolyte cells according to claim 1 or 2 with which said oxide contains a lithium element.

[Claim 4] Positive active material for nonaqueous electrolyte cells according to claim 1 to 3 said whose crystal grain child is a globular form.

[Claim 5] Positive active material for nonaqueous electrolyte cells according to claim 1 to 3 which consists of mixture of the crystal grain child of said oxide who has the particle size of 0.1-2 micrometers, and the aggregated particle of said crystal grain child who has the particle size of 2-20 micrometers.

[Claim 6] Said crystal grain child is positive active material for nonaqueous electrolyte cells according to claim 1 to 5 to which the volume of a unit lattice decreases by oxidation.

[Claim 7] Positive active material for nonaqueous electrolyte cells according to claim 1 to 6 whose error of the ratio of a nickel element and a manganese element is less than 10 atom %.

[Claim 8] Positive active material for nonaqueous electrolyte cells according to claim 3 to 7 with which the lithium element, nickel element, and manganese element which are contained in said oxide fill $0.97 \leq \text{Li}/(\text{nickel}+\text{Mn}) \leq 1.03$.

[Claim 9] The manufacture approach of the positive active material for nonaqueous electrolyte cells of having the process which throws the water solution containing nickel salt and manganese salt, and an alkali solution into coincidence at a reaction vessel, mixes the process which obtains a nickel manganese hydroxide and/or a nickel manganic acid ghost by carrying out coprecipitation of said nickel and manganese, carrying out aeration of the inert gas, said nickel manganese hydroxide and/or a nickel manganic acid ghost, and a lithium compound, and obtains mixture, and the process which calcinates said mixture.

[Claim 10] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 9 that the temperature of said reaction vessel is 30-50 degrees C.

[Claim 11] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 9 or 10 that said nickel salt and manganese salt are a sulfate.

[Claim 12] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 9 to 11 that said alkali solution is the mixture of a sodium hydroxide and aqueous ammonia.

[Claim 13] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 9 to 12 that said lithium compounds are a lithium carbonate and/or a lithium hydroxide.

[Claim 14] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 9 to 13 that the temperature of said baking is 550 degrees C or more.

[Claim 15] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 9 to 13 which the temperature of said baking is 950 degrees C or more, and continues the mixture after baking and is calcinated at 700-780 degrees C.

[Claim 16] The manufacture approach of the positive active material for nonaqueous electrolyte cells of having the process which blends dryly LiOH-H₂O, nickel(OH)₂, and MnOOH which have the particle size of 0.3

micrometers or less, and obtains mixture, and the process which calcinates said mixture.

[Claim 17] The manufacture approach of the positive active material for nonaqueous electrolyte cells according to claim 16 that the aforementioned burning temperature is 550 degrees C or more.

[Claim 18] The negative electrode which contains at least occlusion, the matter which can be emitted, and/or a metal lithium for a lithium ion as a negative-electrode active material, a separator, the positive electrode containing positive active material according to claim 1 to 8, and the nonaqueous electrolyte rechargeable battery that consists of an electrolyte.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive active material for nonaqueous electrolyte cells. Furthermore, this invention relates to a cheap nonaqueous electrolyte rechargeable battery by the high capacity which has a positive electrode containing specific positive active material.

[0002]

[Description of the Prior Art] The request on the cell of small, a light weight, and a high energy consistency has become strong also about the cell which are those power sources for a drive with the spread of an AV equipment cordless and portable in recent years, personal computers, etc. Since especially a lithium secondary battery is a cell which has a high energy consistency, it is expected as a next-generation prime cell, and the potential market size is also large. In most lithium secondary batteries by which current marketing is carried out, although LiCoO₂ which has the high voltage of 4V as positive active material is used, since Co is expensive, the price of LiCoO₂ is high. From this, various positive active material which replaces LiCoO₂ is studied. It seems that a lithium content transition-metals oxide is studied energetically, and commercialization is carried out for LiMn₂O₄ in which LiNi_aCo_bO₂ ($a+b=1$) is promising for, and has Spinel structure especially.

[0003] Moreover, research on nickel and manganese is briskly done as alternate material of expensive cobalt.

For example, LiNiO₂ which has layer structure has large extent of degradation from the crystal structure changing in connection with charge and discharge, although a big discharge capacity is expected. Then, the crystal structure at the time of charge and discharge is stabilized, and adding the element which can control degradation to LiNiO₂ is proposed. Specifically as such an alloying element, elements, such as cobalt, manganese, titanium, and aluminum, are raised. Furthermore, the conventional technique which uses the multiple oxide of nickel and Mn as positive active material for lithium secondary batteries is explained. For example, in U.S. Pat. No. 5393622, after blending dryly the hydroxide of nickel, the hydroxide of Mn, and the hydroxide of Li at once, calcinating them and cooling to a room temperature further, the method of manufacturing the active material which has the presentation which carries out heating baking again and is shown by formula: Li_yNi_{1-x}Mn_xO₂ (the inside of a formula, $0 < x \leq 0.3$, $0 < y \leq 1.3$) is proposed.

[0004] Moreover, in U.S. Pat. No. 5370948, Li salt, nickel salt, and Mn salt are mixed at once in a water solution, and the method of obtaining the active material shown through desiccation and baking by formula: LiNi_{1-x}Mn_xO₂ (the inside of a formula, $0.005 \leq x \leq 0.45$) is proposed. Moreover, in U.S. Pat. No. 5264201, the dry type composition approach of mixing and calcinating the hydroxide of nickel and manganese or oxide, and a superfluous lithium hydroxide, and the synthetic method of obtaining reduced pressure drying and the active material which calcinates and is shown by formula: Li_xNi_{2-x}Mn_yO₂ (the inside of a formula, $0.8 \leq x \leq 1.0$, $y \leq 0.2$), after making the oxide of nickel and manganese etc. into a slurry in the saturated water solution of a lithium hydroxide are proposed. Obtaining the active material shown by formula: LiNi_{1-x}Mn_xO₂ (the inside of a formula, $0 < x \leq 0.2$, $y \leq 0.2$) with the dry-blending synthesis method using beta-nickel (OH)₂ in U.S. Pat. No. 5629110 further again is proposed. Moreover, in JP,8-171910,A, an alkali solution is added into the mixed water solution of manganese and nickel, coprecipitation of manganese and the nickel is carried out, a lithium hydroxide is added, and the method of obtaining the active material shown by formula: LiNi_xMn_{1-x}O₂ (the inside of a formula, $0.7 \leq x \leq 0.95$) is proposed by subsequently calcinating.

[0005] Moreover, in JP,9-129230,A, the desirable particle-like active material which has the presentation shown by formula: LiNi_xM_{1-x}O₂ (the inside of a formula and M are any one or more sorts of Co, Mn, Cr, Fe, V, and

aluminum and $1 > x \geq 0.5$) is indicated, and the thing of $x = 0.15$ is shown as an active material containing nickel and Mn. moreover, in JP,10-69910,A, the active material shown by formula: $\text{Li}_{1-x}\text{Ni}_x\text{Mn}_{1-x}\text{O}_2$ (the inside of a formula and M -- Co, aluminum, Mg, Fe, Mg or Mn, $0 < x \leq 0.5$, and $0 \leq x - 1 < 0.2$, $x = x_1 + x_2$, and $0.9 \leq y \leq 1.3$) compounded with the coprecipitation synthesis method is proposed. If discharge capacity is originally small in said official report and X_2 exceeds 0.5 in it when M is Mn, it is indicated that the original function as positive active material of the lithium secondary battery aiming at high capacity is lost. When Mn ratio is the largest, $\text{LiNi}_0.6\text{Mn}_{0.4}\text{O}_2$ is illustrated [*****]. In addition, in U.S. Pat. No. 5985237, although the manufacture approach of LiMnO_2 which has layer structure is shown, this is a 3V class active material substantially.

[0006] All the advanced technology indicated by the above United States patent official reports and the Japanese patent application public presentation official report adds the element of a minute amount to LiNiO_2 , leaving the description of LiNiO_2 , in order to improve electrochemical properties, such as the cycle property of LiNiO_2 . Therefore, the amount of nickel contained in the active material obtained after addition has always exceeded the amount of Mn, and many ratios of nickel:Mn=0.8:0.2 are proposed. Moreover, nickel:Mn=0.55:0.45 are indicated as a ratio with most amounts of Mn. However, in these conventional technique, since LiNiO_2 dissociates with LiMnO_2 , it is difficult to obtain the multiple oxide which has the crystal structure of a single phase. It is because Mn^{2+} oxidizes in the case of coprecipitation, this tends to become Mn^{3+} and Mn^{3+} cannot form nickel $^{2+}$ and a homogeneous multiple oxide easily.

[0007]

[Problem(s) to be Solved by the Invention] As mentioned above, researches and developments of LiNiO_2 and LiMnO_2 which are the positive active material of low cost in high capacity are made, having the same layer structure as alternate material of LiCoO_2 which has the high voltage of 4V by which current marketing is carried out. However, LiNiO_2 does not have a flat discharge configuration, and its cycle life is also short. Furthermore, thermal resistance is also low and there is a big problem in using it as alternate material of LiCoO_2 . For this reason, although to add and improve various elements to LiNiO_2 is tried, it is still inadequate. Moreover, in LiMnO_2 , since only the electrical potential difference of 3V is obtained, it does not have layer structure but LiMn_2O_4 with Spinel structure with a low capacity is beginning to be studied. Therefore, this invention aims at offering the positive active material which can solve the above problems. Moreover, this invention has the electrical potential difference of 4V equivalent to LiCoO_2 , shows a flat discharge curve, and is to obtain the positive active material of a low price by high capacity from LiCoO_2 further. Furthermore, this invention aims also at offering the nonaqueous electrolyte rechargeable battery which excelled [high capacity / which used this positive active material] in charge-and-discharge effectiveness.

[0008]

[Means for Solving the Problem] This invention consists of a crystal grain child of the oxide which contains the nickel element and manganese element of this ratio substantially, and relates to the positive active material for nonaqueous electrolyte cells whose crystal structure of said crystal grain child is rhombohedron structure (it belongs to a rhombohedral system). If it puts in another way, in said crystal grain child, the nickel atom and the manganese atom will distribute to homogeneity mutually. Said crystal grain child's crystal structure is hexagonal system, and it is effective that the die length of a c-axis is 14.25Å or more. As for said positive active material, it is effective that said oxide contains a lithium element further. It is effective that said crystal grain child is a globular form. Moreover, as for said positive active material, it is effective to consist of mixture of the crystal grain child of said oxide who has the particle size of 0.1-2 micrometers, and the aggregated particle of said crystal grain child who has the particle size of 2-20 micrometers. Moreover, said crystal grain child's crystal structure is rhombohedron structure, and it is effective that it is that to which the volume of a unit lattice decreases by oxidation. Moreover, it is effective that the error of the ratio of a nickel element and a manganese element is less than 10 atom %. Moreover, it is effective that the lithium element, nickel element, and manganese element which are contained in said oxide fill $1.03 \leq \text{Li}/(\text{nickel} + \text{Mn}) \leq 1.03$.

[0009] Furthermore, this invention throws the water solution containing nickel salt and manganese salt, and an alkali solution into coincidence at a reaction vessel, and it relates also to the manufacture approach of the positive active material for nonaqueous-electrolyte cells of having the process which mixes the process which obtains a nickel manganese hydroxide and/or a nickel manganic acid ghost, said nickel manganese hydroxide and/or a nickel manganic acid ghost, and a lithium compound, and obtains mixture, and the process which

calcinate said mixture, by carrying out coprecipitation of said nickel and manganese, carrying out aeration of the inert gas. In this manufacture approach, it is effective that the temperature of said reaction vessel is 30-50 degrees C. Moreover, it is effective that said nickel salt and manganese salt are a sulfate. Moreover, it is effective that said alkali solution is the mixture of a sodium hydroxide and aqueous ammonia. Moreover, it is effective that said lithium compounds are a lithium carbonate and/or a lithium hydroxide. Moreover, it is effective that the temperature of said baking is 550 degrees C or more. Moreover, the temperature of said baking is 950 degrees C or more, and it is effective to continue said mixture after baking and to calcinate at 700-780 degrees C.

[0010] This invention relates also to the manufacture approach of the positive active material for nonaqueous electrolyte cells of having the process which blends dryly $\text{LiOH-H}_2\text{O}$, Ni(OH)_2 , and MnOOH which have the particle size of 0.3 micrometers or less, and obtains mixture, and the process which calcinates said mixture further again. In this case, it is effective that the aforementioned burning temperature is 550 degrees C or more. Moreover, this invention relates to the negative electrode which contains at least occlusion, the matter which can be emitted, and/or a metal lithium for a lithium ion as a negative-electrode active material, a separator, the positive electrode containing the above-mentioned positive active material, and the nonaqueous electrolyte rechargeable battery that consists of an electrolyte. According to this invention, a cheap nickel manganese multiple oxide can be effectively used as positive active material, and a nonaqueous electrolyte rechargeable battery with sufficient charge-and-discharge effectiveness can be offered by high capacity.

[0011]

[Embodiment of the Invention] this invention persons found out not the technique of improving the property which LiNiO_2 has, and the property which LiMnO_2 has by putting in a new alloying element in view of the trouble in the above conventional techniques but the positive active material which consists of a nickel manganese multiple oxide which discovers a new function by making homogeneity distribute a nickel compound and a manganese compound on atomic level, and forming the solid solution. That is, in the conventional technique, although many elements were proposed as an alloying element, it was not [which element is concretely desirable] technically clear in it. On the other hand, this invention persons came to complete a header and this invention for a new function being discovered by combining nickel and manganese by this ratio mostly, as a result of coming research in piles wholeheartedly about the combination and the addition rate of various elements.

[0012] A coprecipitation method is desirable in order to make nickel and manganese dissolve on atomic level. When making it dissolve with a coprecipitation method, the nickel and manganese in the inside of a water solution are divalent ion. It is desirable to carry out coprecipitation by neutralizing with the alkali which existed with the same valence as it is, and was dropped at coincidence. However, in the case of manganese, it is very easy to oxidize, and the dissolved oxygen which recognizes minute amount existence into a water solution will also fully oxidize, and Mn will become trivalent ion. Thus, dissolution of atomic level will become inadequate by divalent ion and trivalent ion being intermingled. In this invention, in order to control such a thing, it is desirable to take the approach of carrying out bubbling of nitrogen, an argon, etc. which are inert gas into a water solution, and removing dissolved oxygen, or adding a reducing agent in a water solution beforehand. Therefore, the difference from the conventional technique of a coprecipitation method is carrying out coprecipitation by the inert atmosphere.

[0013] As for the positive active material concerning this invention, it is desirable that consist of a crystal grain child of the oxide which contains the nickel element and manganese element of this ratio substantially, and said oxide contains a lithium element. Said oxide is a single phase which has layer structure in crystal structure, and belongs to a rhombohedral system, and the nickel atom and the manganese atom are distributing to homogeneity on atomic level. The reason with desirable using combining nickel and manganese is as follows. That is, when said oxide is applied to the positive active material for lithium secondary batteries, Li goes the inside of a crystal in and out by charge and discharge. In the usual active material, the electronic electric conductivity of an active material will fall in the discharge last stage, and a discharge curve will become gently-sloping. This is considered to be polarization caused when electronic electric conductivity falls. However, since the electronic state of each proper interacts when nickel and manganese are combined, it is possible to suppress that electronic electric conductivity falls remarkably in the discharge last stage. As a result, a charge-and-discharge curve becomes a desirable flat configuration.

[0014] A device is required also for the manufacture approach for on the other hand creating the above-mentioned oxide. Usually, when it is going to compound a multiple oxide, a hydroxide, an oxy-hydroxide, or an oxide containing each element etc. is mixed and calcinated. the case where $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ which is the typical presentation of this invention is created -- $\text{LiOH}\cdot\text{H}_2\text{O}$ -- after fully mixing MnOOH by O and nickel (OH) 2 and 2:1:1 (mole ratio), it calcinates at the suitable temperature to which a reaction advances. Explanation that its content of Mn is low also in any, and a dry type synthesis method is enough as it although such a dry-blending synthesis method is indicated by U.S. Pat. No. 5393622, No. 5370948, and No. 5264201 is made. However, when this invention persons used the dry-blending synthesis method concerning the above-mentioned United States patent, it turned out that it is difficult for nickel and manganese to dissolve on atomic level, and a single phase is very hard to be obtained. However, this invention persons found out that a single-phase thing was obtained, when three kinds of above-mentioned mixed powder is very fine particles, for example, as long as it saw only with the X diffraction pattern by using a particle 0.3 micrometers or less.

[0015] Furthermore, according to the following coprecipitation methods, such a dry-blending calcinating method showed that a more ideal oxide was obtained. If a wet coprecipitation method is used in order to create the multiple oxide of nickel, it will become clear by the latest research that a good result is obtained. For example, nickel and a manganese coprecipitation method are indicated by JP,8-171910,A. A coprecipitation method is the technique of settling two elements to coincidence in a water solution using neutralization, and obtaining a compound hydroxide. Since current was little and also only replaced some nickel by the element, the usual coprecipitation method was enough as it. However, in order to make the same quantity of a nickel element and a manganese element dissolve on atomic level substantially like this invention, the advanced technique was required, and by the conventional approach, it was impossible. the case where make the hydroxide and lithium which were obtained with the coprecipitation method react, and the target lithium content multiple oxide is obtained -- the particle shape -- a big difference arises in the electrochemical property at the time of using it for a cell, and control of the difference is difficult for it by the conventional approach.

Moreover, burning temperature should also choose a suitable burning temperature as the electrochemistry property out of doing big effect. An example describes the conditions on such composition in a detail more.

[0016] elements various in order for choosing the combination of nickel and manganese to have a big meaning in this invention and to improve LiNiO_2 like before -- minute amount ***** -- it differs from things. As for the ratio of nickel and manganese, 1:1 is ideal. It is not put in practical use conventionally [of such a ratio / compound]. Furthermore, the synthesis method in this invention improves a coprecipitation method. What is necessary is just to choose the conditions according to the purpose, in order to change to an electrochemistry property, while the particle shape of the active material obtained changes with the conditions of a coprecipitation method, or conditions of subsequent baking.

[0017] (1) Explain the case where positive active material is manufactured with a positive-active-material coprecipitation method. The schematic diagram of the experiment facility used here is shown in drawing 1. The nickel sulfate and the manganese sulfate were used as a raw material. 1.2 mols [/l.] NiSO_4 water solution, the mixed solution of MnSO_4 water solution, a 4.8 mols [/l.] NaOH water solution, and 4.8 mols [/l.] NH_3 solution are respectively thrown into a reaction vessel 1 at the rate of 0.5ml / min at coincidence. The cylinder-like tube 2 is installed into the reaction vessel 1, and it has the rabble 3 in the tube. Although the hydroxide of coprecipitation is obtained in this tube, the force of (the bottom sense of a reaction vessel) is applied downward with the stirring rod currently installed by coincidence in the tube. The microcrystal of the hydroxide obtained by this force collides mutually, carries out crystal growth, and forms a crystal grain child. These particles pass through the outside of a tube, as the arrow head in drawing 1 shows, and they are taken out by overflow out of a system. The particle obtained at this time is substantially spherical by the force of a collision etc.

[0018] At this time, the temperature of a reaction vessel is kept at 30-50 degrees C. Moreover, if oxygen is dissolved in a water solution, manganese will become trivalence from bivalence that it is very easy to oxidize. Therefore, if it is going to obtain $\text{nickel}_{1-x}\text{Mn}_x(\text{OH})_2$ of beta mold, in order to drive out dissolved oxygen of this reaction vessel, it is necessary to carry out bubbling of the inert gas, such as nitrogen or an argon, or, and it is necessary to add a certain reducing agent and to control oxidation of manganese. What is necessary is just to use the dissolved oxygen in liquid well, even if $\text{nickel}_{1-x}\text{Mn}_x(\text{OH})_2$, $x\text{SO}_4^{2-}$, and $y\text{H}_2\text{O}$ of alpha mold are obtained when satisfactory, or on the other hand when you want to manufacture this conversely.

[0019] According to the experiment of this invention persons, the result of an X diffraction image showed that

the higher hydroxide of crystallinity [direction / of about 30-degree C low-temperature field] was obtained. Since such a reaction vessel can moreover manufacture a compound hydroxide continuously at high speed, it is very useful industrially. however, the particle size distribution of the particle obtained -- large -- becoming -- size -- the particle of various particle size will be mixed. Moreover, the bottom of a reaction vessel is covered with a spherical big particle which exceeds 10 micrometers, it is hard coming to take it out and it also has the fault that particle size can seldom be enlarged. Here, the SEM (scan type electron microscope) photograph of the front face of the typical particle obtained by drawing 2 by such reaction vessel was shown. Moreover, the SEM (scan type electron microscope) photograph of the cross section of the typical particle obtained by drawing 3 by such reaction vessel was shown. It is 1000, 3000, 10000, and 30000 times the scale factor of these photographs of this. (a) of (a), (b), and drawing 3 of drawing 2 and (b) show that a particle is substantially spherical. Moreover, the irregularity of a configuration like a rib is in homogeneity in a front face, and (c) of drawing 2 and (d) show that a particle is a porous body further. Moreover, a uniform rib is observed like a front face until it reaches [from the SEM photograph of the cross section of the particle shown in drawing 3] the interior, and it turns out that it is the porous body in which a particle has the hole of homogeneity size mostly. An example of a chemical-analysis (elemental analysis) result of the obtained multiple oxide is shown in Table 1 for reference.

[0020]

[Table 1]

組	成
Ni (%)	31.7
Ni (mol/g)	0.00540
Co (%)	0.054
Fe (%)	0.053
Cu (%)	≤ 0.001
Mn (%)	28.5
Mn (mol/g)	0.00519
Na (%)	0.17
Cl (%)	≤ 0.05
SO ₄ (%)	0.073
タ ッ プ 密 度 (g/cc)	0.65
パ ル ク 密 度 (g/cc)	0.44
粒 径 (μ m)	12.0
Mn : Ni 比	0.98:1.02

[0021] What is necessary is just to change the manufacture approach as follows, in order to obtain a spherical compound hydroxide with a higher-density and big particle size. The schematic diagram showing the configuration of the changed experiment facility is shown in drawing 4 . A mixed solution is introduced into a reaction vessel 6 from a feed hopper 5 using a pump 4, and it is made to collide with the microcrystal which is made to turn a flow up, and coprecipitated and sediments up from under the reaction layer 6 in the facility shown in drawing 4 . The uptake section 7 of an ingredient is formed in the lower part of a facility. Therefore, although the crystal grain child whom the crystal progressed to some extent and specific gravity increased sediments and the lower uptake section 7 is reached, an underdeveloped crystal grain child is put back to the force of the solution by which a flow is carried out from the lower part, and has become the system which does not fall to the lower part.

[0022] Moreover by such approach, tap density can obtain 2.2g /of compound hydroxides of the high density of 3 cm with a big particle size of 10-20 micrometers. Here, the typical SEM photograph of the particle obtained by this approach is shown in drawing 5 . 1000, 2000, and a 20000 times as many SEM photograph as this were shown in (a), (b), and (c) at drawing 5 , respectively. In the particle, unlike the thing of the porosity mentioned above for a while, high density is filled up with microcrystal and the spherical big particle is formed. In addition, although a hydroxide is still satisfactory for a crystal grain child, when aging under preservation poses a problem, it can also be made an oxide by drying and calcinating at low temperature. As mentioned above,

according to this invention, the spherical particle of high density can also manufacture a porosity spherical particle by uniting and changing the conditions of the coprecipitation approach into the purpose. Furthermore, particle size is also controllable free from a small particle size to near 20 micrometer. The crystallinity which can be observed through an X-ray is also controllable by changing the temperature of a reaction vessel suitably.

[0023] $\text{Li}_y\text{Ni}_{1-x}\text{Mn}_x\text{O}_2$ which is the positive active material for lithium secondary batteries made into the purpose is obtained by mixing with sources of a lithium, such as a lithium hydroxide, and next, calcinating the obtained hydroxide or oxide. What is necessary is just to use a lithium hydroxide as a source of a lithium at this time. Although it was possible to have obtained the target single phase when the lithium carbonate was examined, the lithium hydroxide was more advantageous in respect of control of particle shape, crystallinity, etc. It is desirable to supply a lithium even to the interior of a spherical nickel manganese hydroxide at homogeneity. It is ideal, in order that a lithium hydroxide may fuse at low temperature comparatively first, a lithium may be supplied to the interior of a nickel manganese hydroxide particle, temperature may follow subsequently to going up and oxidation reaction may start from the outside of a particle gradually, when a lithium hydroxide is used. On the other hand, when a lithium carbonate is used, decarboxylation must occur once and this reaction is started at an elevated temperature as compared with the case of a lithium hydroxide. Therefore, decarboxylation and oxidation reaction will occur in coincidence mostly. This is considered to be the reason the lithium hydroxide is more advantageous in respect of control of particle shape, crystallinity, etc.

[0024] Below, desirable baking conditions are explained. A lithium hydroxide is fully mixed with a nickel manganese compound hydroxide by dry type. As for a lithium hydroxide and a nickel manganese hydroxide, at this time, it is ideal to mix so that the atomic ratio of Li, nickel, and Mn may fill $\text{Li}/(\text{nickel}+\text{Mn})=1$. However, it can increase a little for control of the temperature of baking, or particle shape, or can also reduce. For example, more some lithiums are mixed [the time of burning temperature being an elevated temperature, and] to enlarge the primary particle after baking. In this case, about 3% of increase and decrease are desirable. The ambient atmosphere of baking should just be an oxidizing atmosphere. Here, the usual atmospheric-air ambient atmosphere examined.

[0025] The temperature of baking is important. The X diffraction image of the lithium content nickel manganic acid ghost obtained when it calcinated at each temperature to drawing 6 is shown. Firing time was fixed with 15 hours. (a) of drawing 6, (b), (c), (d), (e), and (f) inquired with the burning temperature exceeding ***** 550, 650, 750, 850, and 1000 and 1050 degrees C. It turns out that the ingredient which had the almost same structure in this range can be manufactured. About crystallinity, although calcinated more at the elevated temperature, the peak of an X diffraction is Sharp, and it turns out that crystallinity is high. The pyrolysis of an ingredient etc. is not produced at the elevated temperature exceeding 1000 degrees C, either. Moreover, when the crystal structure is analyzed from this X diffraction pattern, it turns out that it belongs to a rhombohedral system.

[0026] Moreover, this was changed into hexagonal system and Miller-indices attachment was performed. It turns out that all peaks can belong Miller indices and the single phase is formed. However, it is more desirable to drop temperature on about 750 degrees C again, and to apply re-baking, after calcinating at 1000 degrees C, in order to return this oxygen element to an ingredient, since it is considered that the oxygen on the front face of an ingredient is also missing a little when calcinating at the temperature exceeding 1000 degrees C. Therefore, that what is necessary is just 550 degrees C or more, burning temperature is 950 degrees C or more still more preferably, and is 1000 degrees C or more still more preferably 850 degrees C or more preferably. Furthermore, in the case of 950 degrees C or more, it is desirable to once drop temperature near 750 degree C, and to carry out 2nd baking.

[0027] The particle shape of the lithium content nickel manganic acid ghost calcinated and obtained was observed by SEM. The SEM photograph of a typical particle is shown in (a) of drawing 7. From drawing, the particle has stopped the shape of a ball. It turns out that this particle is what primary particles 1 micrometer or less gather, and constitutes the about 10-micrometer spherical aggregated particle. Moreover, as the front face of a primary particle is shown in (b) of drawing 7, it turns out that it comes out smoothly and fills up densely. Moreover, by controlling the conditions of burning temperature or others, as shown in (d) of (c) and drawing 8 of drawing 7, and (e), partial collapse of an aggregated particle, change in the particle diameter of a primary particle, and form status change-ization are enabled. Still as shown in (e) of drawing 8, the ingredient which consists only of the first [about] particle can also be obtained. Here, the data of the ingredient manufactured

not by coprecipitation but by the usual dry-blending calcinating method for the comparison are shown. Here, nickel (OH)₂ and MnOOH which have the particle size of several micrometers, and a LiOH-H₂O particle were mixed so that it might become a predetermined presentation, and it calcinated in the atmospheric-air ambient atmosphere similarly for 15 hours. Burning temperature was made into 850 or 1000 degrees C. The X diffraction peak of the obtained ingredient is shown in (a) and drawing 10 (a) of drawing 9. The peak of the ingredient obtained with 850 or a 1000-degree C coprecipitation method by (b) of drawing 9 and (b) of drawing 10 is shown in the bottom. It turns out that the peak is carrying out the split and the single phase is not formed from these drawings about what was obtained by the dry-blending method. And the fall of electrochemistry properties, such as charge-and-discharge capacity and a cycle life, is expected because it is not a single phase. When this originated in manganese fully not being mixed with nickel on atomic level, for the ***** reason, it made fine particle size of nickel (OH)₂ and MnOOH to be used, and LiOH-H₂O, and added examination. Consequently, when particle about 0.3 micrometers or less was used, it was able to check that a single phase was formed mostly with the X-ray.

[0028] Below, the electrochemistry property of the obtained ingredient is explained. As shown in drawing 6, the electrochemistry property of the ingredient obtained with the burning temperature of 550-1050 degrees C was evaluated by producing a coin mold cell. The coin mold cell was produced in the following procedures. The polyvinylidene fluoride resin (henceforth "PVDF") which is the acetylene black and the binder which are the positive active material obtained with each burning temperature and electric conduction material is mixed by the weight ratio of 80:10:10, and a sheet-like moldings is obtained. And pierced this moldings disc-like, it was made to dry at the temperature of 80 degrees C in a vacuum for about 15 hours, and the positive electrode was obtained. Moreover, the lithium metal fabricated in the shape of a sheet was pierced disc-like, and it considered as the negative electrode. The electrolytic solution dissolved and prepared one-mol LiPF₆ to the mixed solvent of EC (ethylene carbonate) and EMC (ethyl methyl carbonate)1:3 (volume ratio), using the fine porosity film of polyethylene as a separator. And the coin mold cell of 2016 sizes (a path is 20mm and the thickness of 1.6mm) was produced with the conventional method using these.

[0029] Charge and discharge were repeated between 3.0-4.5V with the constant current value of the rate of 10 time amount using the produced coin mold cell. In any case, the charge-and-discharge capacity of 150 or more mAh/g could be obtained the first stage, and it was found by that discharge voltage is 4V class. However, it became clear with burning temperature that there is a difference in the configuration and cycle life of some charge-and-discharge curves. Two patterns of the typical thing were shown in drawing 11. By the case where it calcinates at 750 degrees C, (a) of drawing 11 shows the charge-and-discharge property at the time of calcinating (b) at 1000 degrees C. The coin mold cell using the ingredient which, on the other hand, calcinated the coin mold cell using the ingredient calcinated at each temperature of 550-750 degrees C above 850 degrees C by the almost same behavior as (a) was the almost same behavior as (b). Although charge-and-discharge capacity is fully obtained as shown in drawing in (a), the configuration of a discharge curve is gently-sloping, it is lacking in surface smoothness, and the capacity reduction accompanying a cycle is large. That is, it turns out that a cycle life falls. On the other hand, in (b), sufficient charge-and-discharge capacity is obtained, and a cycle life with it is acquired. [there is little degradation accompanying a cycle and still better / the configuration of a discharge curve is flat, and] It is thought that such a difference has the close relation to development of crystallization.

[0030] Although the X diffraction pattern corresponding to each burning temperature was shown in drawing 6, it turns out that what was calcinated and obtained above 850 degrees C shows a sharp peak, and crystallization is progressing. Therefore, when it has the configuration of a flat discharge curve and a cell with a good cycle life is desired, burning temperature should be made 850 degrees C or more. Generally, although 600-900 degrees C was made desirable, as were shown in United States patent 5370948th and No. 5629110 till the former, and burning temperature was shown in drawing 11, also on 1000-degree C baking conditions, in any way, it was satisfactory and a result with the more desirable baking at an elevated temperature was brought rather. However, it is more desirable to drop about 750 degrees C of temperature again, and to apply re-baking after 1000-degree-C baking, in order to return this oxygen element to an ingredient, since it is considered that the oxygen on the front face of an ingredient is also missing a little when calcinating at the temperature exceeding 1000 degrees C, as mentioned above.

[0031] Next, crystal structure change was measured for the purpose of the analysis of the reaction mechanism

accompanying the charge-and-discharge reaction of this ingredient. The experiment was conducted by producing the above-mentioned coin mold cell. What produced with the coprecipitation method and was calcinated at 1000 degrees C as a positive-active-material ingredient was used. Charge and discharge were interrupted at each way middle point of charge and discharge, the coin mold cell was disassembled, and crystal structure change of an ingredient was analyzed using X-ray diffractometer. The positive electrode which disassembled and took out the coin mold cell also contains PVDF which is acetylene black and the binder which are an electric conduction agent. In addition, in order to make decomposition under measurement, and effect of moisture into the minimum, analysis was put into the bag made from polyethylene, and was performed. The result of an X diffraction is shown in drawing 12. The value of "mAh/g" shown all over drawing shows each oxidation degree. Therefore, it means that the electrochemical oxidation of an ingredient is advancing as it goes to the lower part (from (a) to (g)) of drawing 12. If oxidation shows that Li ion falls out from an ingredient and transposes it to a cell, it means that charge is advancing. Moreover, the crystal structure belongs to a rhombohedral system. It asked for the lattice constant (a, c) in hexagonal system, after changing this into hexagonal system and performing Miller-indices attachment. a and c are a-axis Cho and c-axis Cho of a unit lattice. It turns out that the oxidation process is advancing maintaining the single phase of hexagonal system without crystal system changing a lot so that more clearly than drawing 12.

[0032] An a-axis and a c-axis change with oxidation. The situation of this change is shown in drawing 13. In drawing 13, O is a c-axis and ** is an a-axis. Moreover, the volume change of the unit lattice calculated from a-axis Cho and c-axis Cho is shown in drawing 14. A c-axis decreases through the maximal value, after increasing gradually with oxidation (O in drawing 13). The value of this c-axis is also large as compared with a value as shown in U.S. Pat. No. 5393622. Manganese is mixed with nickel by about 1:1 atomic ratio, and this also forms the solid solution, and is considered to originate in having discovered a new function. An a-axis falls gradually with oxidation and change stops at constant value after that (** in drawing 13). On the other hand, the grid volume decreases linearly with oxidation (drawing 14). This has big value. In the fuel cell subsystem which is mainly concerned with current and a lithium secondary battery, LiCoO₂ is used for a positive electrode and graphite is used for the negative electrode. The grid volume increases LiCoO₂ of a positive electrode with oxidation. It expands because graphite also inserts Li ion between layers. Therefore, in this fuel cell subsystem, a positive electrode and a negative electrode expand with charge. This expansion is inconvenient in a cell, and by expansion, a separator is crushed or it specifically causes an internal short circuit by the case. Moreover, the cure of reducing restoration capacity beforehand in consideration of such expansion may be required. Furthermore, in the case where it applies to a thin cell, the cell itself will expand and a thin merit may be erased. However, if the active material to which the grid volume decreases by oxidation can be used, it becomes possible to absorb expansion of a negative electrode to some extent, and un-arranging according to the expansion as the whole cell can be solved. Therefore, completely as opposed to the ingredient which expands by charge like LiCoO₂, the ingredient of this invention to which the volume decreases by charge is worthy, especially when using the ingredient which expands by charge of graphite etc. as a negative electrode.

[0033] Below, the discharge potential of this ingredient or the configuration of a discharge curve is explained. LiCoO₂ (a) and the discharge curve of LiNiO₂ (b) are shown in drawing 15, and LiNi₁/2Mn₁/2O₂ (c), and the discharge curve of LiMnO₂ (d) are shown in drawing 16. The discharge curve of LiNi_{1-x}Mn_xO₂ of this invention is flatter than the discharge curve of LiNiO₂. Moreover, as compared with LiMnO₂, charge and discharge voltage differs clearly. It turns out that a different new function from both of the descriptions is discovered by making nickel and manganese dissolve by the almost equivalent ratio so that clearly also from this. Therefore, in order to improve this taking advantage of the description of LiNiO₂ like before, the purpose also differs also from a result greatly to the research which looked for various alloying elements. Here, drawing on which the discharge curve to 30 cycle was drawn in piles is shown about the case where LiNi₁/2Mn₁/2O₂ is used for drawing 17. In this case, charge is set to 4.3V. It turns out that there is also almost no degradation of capacity, without the configuration of a discharge curve changing in connection with a cycle so that more clearly than drawing. if the ratio of nickel and manganese shifts from 1:1 -- the description of the element of the direction with many contents -- a color -- although it comes to come out deeply, if it is a gap of about 10%, the new description of this nickel manganese will be maintained. Therefore, on the occasion of manufacture of an ingredient, it should be compounded by this precision within the limits.

[0034] In addition, research on this invention has been advanced focusing on LiNi_{1-x}Mn_xO₂. And it became

clear to discover a new function because nickel and manganese dissolve by this ratio substantially. It can predict easily that added value is acquired by adding a still newer alloying element into these ingredients. For example, the ingredient expressed with chemical formula: $\text{LiNi}_{1-x}\text{Mn}_x\text{AzO}_2$ is raised. For example, it is expected by A that the thermal stability of the ingredient obtained is improvable by carrying out optimum dose addition of aluminum, magnesium, calcium, or the strontium. Moreover, it is expected that an improvement of a cycle life and polarization can be aimed at by adding other transition metals to A. Furthermore, it is also expected that coincidence improves each effectiveness by combining these elements.

[0035] Hereafter, when producing the lithium secondary battery using the positive electrode of this invention, other usable components are described. the positive electrode used in order to produce the positive electrode in this invention -- a mixture -- if an inner electric conduction agent is an electronic conduction nature ingredient which does not cause a chemical change in the constituted cell, there will be especially no limit. For example, graphite, such as natural graphites (scale-like graphite etc.) and an artificial graphite Acetylene black, KETCHIEN black, channel black, furnace black, Conductive fiber, such as carbon black, such as lamp black and thermal black, a carbon fiber, and a metal fiber Metal powder, such as fluoride carbon, copper, nickel, aluminum, and silver These which can raise organic conductivity ingredients, such as conductive metallic oxide, such as conductive whiskers, such as a zinc oxide and potassium titanate, and titanium oxide, and a polyphenylene derivative, etc. are independent, respectively. Or it can mix and use for arbitration in the range which does not spoil the effectiveness of this invention. Also in these, an artificial graphite, acetylene black, and especially nickel powder are desirable. Although especially the addition of an electric conduction agent is not limited, its 1 - 50 % of the weight is especially desirable, and its 1 - 30 % of the weight is desirable. In carbon or especially graphite, 2 - 15 % of the weight is desirable.

[0036] the positive electrode in this invention -- a mixture -- the decomposition temperature of an inner desirable binder is a polymer 300 degrees C or more. For example, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVDF), a tetrafluoroethylene-hexafluoro ethylene copolymer, A tetrafluoroethylene-hexafluoropropylene copolymer (FEP), A tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), A vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-chlorotrifluoroethylene copolymer, An ethylene-tetrafluoroethylene copolymer (ETFE resin), polychlorotrifluoroethylene resin (PCTFE), A vinylidene fluoride-pentafluoropropylene copolymer, a propylene-tetrafluoroethylene copolymer, An ethylene-chlorotrifluoroethylene copolymer (ECTFE), A vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene copolymer, a vinylidene fluoride-perfluoromethylvinylether-tetrafluoroethylene copolymer, etc. can be raised. These can be mixed and used for arbitration in the range which is independent, respectively or does not spoil the effectiveness of this invention. Especially, this most desirable is polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE).

[0037] If it is the electronic conductor which does not cause a chemical change in the constituted cell as a charge collector of a positive electrode, there will be especially no limit. As an ingredient which constitutes a charge collector, the complex made to process carbon, nickel, titanium, or silver can be used for the front face of the others and aluminum which are stainless steel, nickel, aluminum, titanium, various alloys, carbon, etc., for example, or stainless steel. Especially, aluminum or an aluminium alloy is desirable. The front face of these ingredients can also be oxidized. Moreover, irregularity may be attached to a current collection body surface by surface treatment. As a configuration, it may be adopted in the field of a cell, and a foil, a film, a sheet, the thing netted and punched, a lath object, a porous body, foam, a fiber group, a nonwoven fabric, etc. are raised. Although especially thickness is not limited, a 1-500-micrometer thing is used preferably.

[0038] (2) As a negative-electrode ingredient used by negative-electrode active material this invention, a lithium, a lithium alloy, an alloy, an intermetallic compound, carbon, an organic compound, an inorganic compound, a metal complex, an organic high molecular compound, etc. should just be occlusion and a compound which can be emitted about a lithium ion. These can be combined and used for arbitration in the range which is independent or does not spoil the effectiveness of this invention, respectively. As a lithium alloy, Li-aluminum system alloys (U.S. Pat. No. 4,002,492 number etc.), a Li-aluminum-Mn system alloy, a Li-aluminum-Mg system alloy, a Li-aluminum-Sn system alloy, a Li-aluminum-In system alloy, a Li-aluminum-Cd system alloy, a Li-aluminum-Te system alloy, a Li-Ga system alloy (JP,60-257072,A), a Li-Cd system alloy, a Li-In system alloy, a Li-Pb system alloy, a Li-Bi system alloy, a Li-Mg system alloy, etc. are raised. In this case, as for the content of a lithium, it is desirable that it is 10 % of the weight or more.

[0039] As an alloy and an intermetallic compound, the compound of transition metals and silicon, the compound of transition metals and tin, etc. are raised, and especially the compound of nickel and silicon is desirable. As a carbonaceous ingredient, the carbon with which corks, pyrolytic carbon, a natural graphite, an artificial graphite, a meso carbon micro bead, a graphitization mesophase microsphere, vapor growth carbon, glassy carbon, a carbon fiber (a polyacrylonitrile system, a pitch system, a cellulose system, vapor growth carbon system), indeterminate form carbon, and the organic substance were calcinated is raised. These may be combined and used for arbitration in the range which is independent or does not spoil the effectiveness of this invention, respectively. Especially, graphite ingredients, such as what graphitized the mesophase microsphere, a natural graphite, and an artificial graphite, are desirable. In addition, different-species compounds, such as O, B, P, N, S, SiC, and B₄C, may also be included in a carbonaceous ingredient besides carbon. As a content, 0 - 10 % of the weight is desirable.

[0040] As an inorganic compound, a tin compound, a silicon compound, etc. are raised, for example, and a titanate-acid ghost, a tungstic-acid ghost, a molybdic-acid ghost, a niobic acid ghost, a barium salt ghost, a ferric acid ghost, etc. are raised as an inorganic oxide, for example. Moreover, as inorganic chalcogenide, an iron sulfide, a molybdenum sulfide, a titanium sulfide, etc. are raised, for example. As an organic high molecular compound, high molecular compounds, such as the poly thiophene and polyacetylene, are raised, for example, and a cobalt nitride, a copper nitride, a nickel nitride, an iron nitride, a manganese nitride, etc. are raised as a nitride, for example. These negative-electrode ingredients may be combined and used, for example, can consider the combination of carbon and an alloy, or the combination of carbon and an inorganic compound. The mean particle diameter of the carbon material used by this invention has desirable 0.1-60 micrometers. It is 0.5-30 micrometers more preferably. As for specific surface area, it is desirable that it is 1-10m²/g. The magnitude (LC) of the microcrystal of the direction of a c-axis has [a crystal structure top / spacing (d002) of a carbon hexagon-head flat surface] a graphite 100A or more desirable [moreover,] at 3.35-3.40A.

[0041] In this invention, since Li contains in positive active material, the negative-electrode ingredients (carbon etc.) which do not contain Li can be used. Moreover, when the negative-electrode material which does not contain such Li is made to contain a little (for it to be 0.01 - 10 weight section extent to the negative-electrode ingredient 100 weight section) Li, even if a part of Li(s) react with an electrolyte etc. and serve as inactive, since it can supply with Li which the above-mentioned negative-electrode ingredient was made to contain, it is desirable. As mentioned above, it is good, in order to make a negative-electrode ingredient contain Li, for example, if the lithium metal heated and fused is applied on the charge collector which stuck the negative-electrode ingredient by pressure, Li is infiltrated into negative-electrode material, or a lithium metal is beforehand stuck by sticking by pressure etc. into an electrode group and Li is made to dope in a negative-electrode ingredient electrochemically in the electrolytic solution. a negative electrode -- a mixture -- an inner electric conduction agent -- a positive electrode -- a mixture -- like an inner electric conduction agent, if it is the electronic conduction nature ingredient which does not cause a chemical change in the constituted cell, there will be especially no limit. Moreover, since the carbonaceous ingredient itself has electronic conduction nature when using a carbonaceous ingredient for a negative-electrode ingredient, even if it contains an electric conduction agent, it is not necessary to carry out.

[0042] a negative electrode -- a mixture -- as an inner binder, although you may be any of thermoplastics and thermosetting resin, the decomposition temperature of a desirable binder is a polymer 300 degrees C or more. For example, polyethylene, polypropylene, polytetrafluoroethylene (PTFE), Polyvinylidene fluoride (PVDF), styrene butadiene rubber, a tetrafluoroethylene-hexafluoropropylene copolymer (FEP), A tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA), A vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-chlorotrifluoroethylene copolymer, An ethylene-tetrafluoroethylene copolymer (ETFE resin), polychlorotrifluoroethylene resin (PCTFE), A vinylidene fluoride-pentafluoropropylene copolymer, a propylene-tetrafluoroethylene copolymer, An ethylene-chlorotrifluoroethylene copolymer (ECTFE), A vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene copolymer, a vinylidene fluoride-perfluoromethylvinylether-tetrafluoroethylene copolymer, etc. can raise. They are styrene butadiene rubber and polyvinylidene fluoride more preferably. Styrene butadiene rubber is the most desirable especially.

[0043] If it is the electronic conductor which does not cause a chemical change in the constituted cell as a charge collector of a negative electrode, there will be especially no limit. As an ingredient which constitutes a charge collector, a thing, an aluminum-Cd alloy, etc. which were processed with carbon, nickel, titanium, or

silver are used for the front face of the others and copper which are stainless steel, nickel, copper, titanium, carbon, etc., for example, or stainless steel. Especially, copper or a copper alloy is desirable. You may oxidize the front face of these ingredients. Moreover, irregularity may be attached to a current collection body surface by surface treatment. A foil, a film, a sheet, the thing netted and punched, a lath object, a porous body, foam, the Plastic solid of a fiber group, etc. are used like the case of the above-mentioned positive electrode by the configuration. Although especially thickness is not limited, a 1-500-micrometer thing is used preferably. an electrode -- a filler besides an electric conduction agent or a binder, a dispersant, an ion electric conduction agent, a pressure enhancement agent, and other various additives can be used for a mixture. In the constituted cell, a filler can be used anything, if it is the fibrous ingredient which does not cause a chemical change. Usually, fiber, such as olefin system polymers, such as polypropylene and polyethylene, glass, and carbon, is used. Although especially the addition of a filler is not limited, 0 - 30 % of the weight is desirable.

[0044] The positive electrode and negative electrode in this invention may have the protective layer introduced for the purpose of the mechanical protection of the under coat introduced for the purpose other than the binder layer containing positive active material or a negative-electrode ingredient, such as amelioration of the adhesion of a charge collector and a binder layer, conductivity, a cycle property, and charge-and-discharge effectiveness, or a binder layer, or chemical protection. This under coat and protective layer can contain a binder, an electric conduction agent particle, a particle without conductivity, etc.

[0045] (3) As a separator separator, it has big ion transmittance, and has a predetermined mechanical strength, and an insulating fine porosity thin film is used. Moreover, it is desirable to have the function to blockade a hole above 80 degrees C and to raise resistance. Independent, or the sheets and nonwoven fabrics which were built with a combined olefin system polymer or a glass fiber, such as polypropylene and polyethylene, are used from organic solvent-proof nature and hydrophobicity. As for the aperture of a separator, it is desirable that it is the range which an active material, a binder, an electric conduction agent, etc. from which it was desorbed from the electrode sheet do not penetrate, for example, it is desirable that it is 0.1-1 micrometer. Generally the thickness of a separator is used preferably 10-300 micrometers. Moreover, although a void content is determined according to the permeability, the material, and film pressure of an electron or ion, it is desirable that it is generally 30 - 80%. Moreover, if fire retarding materials, such as a glass metallurgy group oxide film, and an incombustible material are used, the safety of a cell will improve more.

[0046] (4) The nonaqueous electrolyte in nonaqueous electrolyte this invention consists of a solvent and lithium salt which dissolves in the solvent. the non-cyclic ester from which, as for a solvent presentation, at least two or more sorts of residue differs, including the un-annular carbonate (for example, ethyl methyl carbonate) of an unsymmetrical form -- as a solvent -- including (for example, dimethyl carbonate and diethyl carbonate being included or dimethyl carbonate and ethyl propionate being included) -- those examples and solvents which are alike other than this and are used are illustrated below. To the ester used for a non-aqueous solvent, for example, ethylene carbonate (EC), Annular carbonate, such as propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC), Dimethyl carbonate (DMC), diethyl carbonate (DEC), Un-annular carbonate, such as ethyl methyl carbonate (EMC) and dipropyl carbonate (DPC), gamma-lactone, such as aliphatic series carboxylate, such as methyl formate (MF), methyl acetate (MA), methyl propionate (MP), and ethyl propionate (MA), and gamma-butyrolactone (GBL), etc. is raised. Especially as cyclic ester, EC, PC, GBL, etc. are desirable and it is desirable that un-annular carbonate, such as DMC, DEC, and EMC, is included as non-cyclic ester. Moreover, what contains aliphatic series carboxylate if needed is desirable. The thing of the whole solvent weight more preferably included for aliphatic series carboxylate in 20% or less of range 30% or less is desirable.

[0047] The solvent of the electrolytic solution of this invention moreover, besides the above-mentioned ester being included 80% or more Non-cyclic ether, such as 1, 2-dimethoxyethane (DME), 1, and 2-diethoxy ethane (DEE) and ethoxy methoxyethane (EME), Cyclic ether, such as a tetrahydrofuran and 2-methyl tetrahydrofuran, Dimethyl sulfoxide, 1, 3-dioxolane, a formamide, an acetamide, Dimethylformamide, dioxolane, an acetonitrile, propyl nitril, Nitromethane, ethyl mono-glyme, trialkyl phosphate, trimethoxy methane, A dioxolane derivative, a sulfolane, a methyl sulfolane, 1,3-dimethyl-2-imidazolidinone, Aprotic organic solvents, such as 3-methyl-2-oxazolidinone, a propylene carbonate derivative, a tetrahydrofuran derivative, ethyl ether, 1, 3-propane ape ton, an anisole, dimethyl sulfoxide, and N-methyl pyrrolidone, may also be included.

[0048] As lithium salt which dissolves in these solvents For example, LiClO₄, LiBF₄, LiPF₆, LLiAlCl₄,

LiSbF₆, LiSCN, LiCl, LiCF₃SO₃, LiCF₃CO₂, Li (CF₃SO₂)₂, LiAsF₆ and LiN (CF₃SO₂)₂, LiB₁₀Cl₁₀ (JP,57-74974,A), A low-grade aliphatic-carboxylic-acid lithium (JP,60-41773,A), LiCl, LiBr, LiI (JP,60-247265,A), A chloro borane lithium (JP,61-165957,A), 4 phenyl lithium borate (JP,61-214376,A), Imide, such as LiN (CF₃SO₂) (C₂F₅SO₂), LiN (CF₃SO₂)₂, LiN (C₂F₅SO₂)₂, and LiN (CF₃SO₂) (C₄F₉SO₂), can be raised. These can be used for the electrolytic solution to be used in the range which is independent, respectively or does not spoil the effectiveness of this invention, combining them with arbitration. Especially, it is more desirable to include especially LiPF₆.

[0049] In this invention, especially desirable nonaqueous electrolyte is the electrolytic solution which contains LiPF₆ as lithium salt, including ethylene carbonate and ethyl methyl carbonate at least. Moreover, when using GBL as a main solvent, it is desirable to add additives, such as VC, several% and to use the mixed salt of LiBF₄ and LiN (C₂F₅SO₂)₂ other than LiPF₆ as lithium salt. Although especially the amount that adds these electrolytic solutions in a cell is not limited, its ***** for initial complements is good by positive active material, the amount of a negative-electrode ingredient, or the size of a cell. Although especially the amount of dissolutions to the non-aqueous solvent of lithium salt is not limited, its l. is desirable in 0.2-2 mols /. Especially, it is more desirable that it is 0.5-1.5 mols/l. Moreover, organic additives, such as 2-methyl furan, a thiophene (JP,61-161673,A), a pyrrole (JP,3-59963,A), an aniline (JP,60-79677,A), crown ether, a pyridine, a triethyl FOSU fight, triethanolamine, cyclic ether, ethylenediamine, n-glyme, hexalin acid TORIAMIDO, a nitrobenzene derivative, and a nitrogen-containing aromatic heterocycle compound (JP,9-204932,A), may be dissolved in the above-mentioned electrolytic solution in order to acquire a good charge-and-discharge property. It is usually used for them, making separators, such as a porous polymer, a glass filter, and a nonwoven fabric, sink in or fill up with this electrolytic solution.

[0050] Moreover, in order to make the electrolytic solution into incombustibility, a halogen-containing solvent, for example, a carbon tetrachloride, and a 3 fluoridation ethylene chloride can be included in the electrolytic solution. Moreover, in order to give fitness to elevated-temperature preservation, carbon dioxide gas can be included in the electrolytic solution. Moreover, the following solid electrolytes can also be used besides liquid. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The nitride of Li, the halogenide, the oxygen acid salt, etc. are well known by the inorganic solid electrolyte. Especially, Li₄SiO₄, Li₄SiO₄-LiI-LiOH, xLi₃PO₄-(1-x) Li₄SiO₄, Li₂SiS₃, Li₃PO₄-Li₂ S-SiS₂, a phosphorus sulfide compound, etc. are effective. In an organic solid electrolyte, polymer ingredients, such as polyethylene oxide, polypropylene oxide, polyphosphazene, the poly aziridine, a polyethylene sulfide, polyvinyl alcohol, polyvinylidene fluoride, poly hexafluoropropylene, etc. these derivatives, mixture, and complex, are effective, for example. Moreover, the gel electrolyte which made the organic solid electrolyte contain the above-mentioned nonaqueous electrolyte can also be used. As the above-mentioned organic solid electrolyte, macromolecule matrix materials, such as polyethylene oxide, polypropylene oxide, polyphosphazene, the poly aziridine, a polyethylene sulfide, polyvinyl alcohol, polyvinylidene fluoride, poly hexafluoropropylene, etc. these derivatives, mixture, and complex, are effective, for example. Especially, the mixture of vinylidene fluoride, the copolymer of hexafluoropropylene and polyvinylidene fluoride, and polyethylene oxide is desirable.

[0051] As a configuration of a cell, a coin mold, a carbon button mold, a sheet mold, cylindrical, flat, a square shape, etc. are applicable to all. The configuration of a cell is compressed into the configuration of a pellet at the time of a coin mold or a carbon button mold, and the mixture of positive active material or a negative-electrode ingredient is mainly used. What is necessary is for the magnitude of a cell just to determine the thickness and the diameter of the pellet. Moreover, when the configurations of a cell are a sheet mold, cylindrical, and a square shape, on a charge collector, the mixture of positive active material or a negative-electrode ingredient is applied, (coat) dried and compressed, and is mainly used. A general approach can be used for the method of application. For example, the reverse roll method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, the casting method, a dip method, the squeeze method, etc. can be raised. The blade method, the knife method, and the extrusion method are desirable also in it. As for spreading, it is desirable to carry out the rate for 0.1-100m/. Under the present circumstances, according to the solution physical properties of a mixture, and drying, the surface state of a good spreading layer can be acquired by selecting the above-mentioned method of application. The time of one side [every] ** or double-sided coincidence is sufficient as spreading. Moreover, it is desirable to prepare

a spreading layer in the both sides of a charge collector, and you may consist of two or more layers in which the spreading layer of one field contains a binder layer. A binder layer contains a binder, an electrical conducting material, etc. like positive active material or a negative-electrode ingredient other than the matter in connection with insertion and emission of a lithium ion. You may have the protective layer which does not contain the active material other than a binder layer, the under coat prepared on a charge collector, the interlayer prepared between binder layers. As for the layer which does not have these active materials, it is desirable that a conductive particle, an insulating particle, and a binder are included. Moreover, continuation, an intermission, or a stripe is sufficient as the method of application. Although the thickness, die length, and width of the spreading layer are decided with the magnitude of a cell, the thickness of the spreading layer of one side is in the condition of having been compressed after dry, and especially its 1-2000 micrometers are desirable.

[0052] The approach generally adopted can be used as a pellet, or desiccation of a sheet or the dehydration approach. Especially, it is desirable independent or to combine and to use hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and a damp wind. The range of temperature of 80-350 degrees C is desirable, and it is especially desirable. [of the range which is 100-250 degrees C] moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or an electrolyte, respectively in respect of cycle nature. Although the approach generally adopted can be used for the method of pressing a sheet, a die-press method and its calender pressing method are especially desirable. Although especially press ** is not limited, its 0.2 - 3 t/cm² is desirable. The pressing speed of the calender pressing method has the amount of desirable 0.1-50m/. Press temperature has desirable room temperature -200 degree C. As for the ratio of the width of face of the positive-electrode sheet to a negative-electrode sheet, 0.9-1.1 are desirable. Especially, 0.95-1.0 are desirable. the content ratio of positive active material and a negative-electrode ingredient -- a compound class and a mixture -- although it cannot limit since it changes with formulas, it can be set as the optimal value in the viewpoint of capacity, cycle nature, and safety. In addition, the winding objects of the electrode in this invention may be the prismatic form configurations where it is not necessary to be necessarily a perfect circle cartridge, and the cross section is an ellipse, such as an ellipse cartridge and a rectangle.

[0053]

[Example] Although an example is represented in below and this invention is explained to it, this inventions are not these things limited to seeing.

The <<example 1 and example of comparison 1>> Outline drawing of longitudinal section of the cylindrical cell produced in this example to drawing 18 is shown. The group of electrode 14 around which the positive-electrode plate and the negative-electrode plate were wound in the shape of a multiple-times swirl through the separator is contained in the cell case 11. And from the positive-electrode plate, the positive-electrode lead 15 is pulled out and it connects with the obturation plate 12, and from the negative-electrode plate, the negative-electrode lead 16 is pulled out and it connects with the pars basilaris ossis occipitalis of the cell case 11. A metal and an alloy with the electronic conduction nature of organic-proof electrolytic-solution nature can be used for a cell case or a lead plate. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used. Especially for a cell case, what processed the stainless steel plate and the aluminum-Mn alloy plate, and a positive-electrode lead are aluminum, and a negative-electrode lead has the most desirable nickel. Moreover, it is also possible to use for a cell case what various engineering plasticses, and this and a metal used together in order to attain lightweight-ization.

[0054] The insulating ring 17 is formed in the vertical section of a group of electrode 14, respectively. And the electrolytic solution is poured in and a cell case is sealed using an obturation plate. At this time, a relief valve can be prepared in an obturation plate. It may be equipped with the various insurance components known from the former besides a relief valve. For example, a fuse, bimetal, a PTC component, etc. are used as an overcurrent-protection component. Moreover, the approach of making a cut in a cell case, the gasket crack approach, the obturation plate crack approach, or cutting process with a lead plate can be used for everything but a relief valve as a cure of an internal pressure rise of a cell case. Moreover, the protection network which built overcharge and the cure against overdischarge into the battery charger may be made to provide, or you may make it connect independently.

[0055] Moreover, the method which intercepts a current by the rise of cell internal pressure can be provided as a cure against overcharge. At this time, the compound which raises internal pressure can be included in a mixture

or an electrolyte. as the compound which raises internal pressure -- Li2 -- carbonates, such as CO₃, LiHCO₃, Na₂CO₃, and NaHCO₃, CaCO₃, MgCO₃, etc. are raised. Well-known approaches (electric welding of an example, a direct current, or an alternating current, laser welding, or ultrasonic welding) can be used for the welding process of a cap, a cell case, a sheet, and a lead plate. Moreover, the compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation. The positive-electrode plate was produced as follows. The carbon powder 10 weight section of an electric conduction agent and the polyvinylidene fluoride resin 5 weight section of a binder are mixed to the positive-active-material powder 85 weight section of this invention. After making dehydration N-methyl pyrrolidinone distribute these, obtaining a slurry, applying on the positive-electrode charge collector which consists of aluminium foil and drying and rolling out, it cuts in predetermined magnitude.

[0056] A negative-electrode plate makes a carbonaceous ingredient the charge of a principal member, and after plastering both sides of copper foil with what was mixed at a rate of 100:5 by the weight ratio, drying and rolling out this and a styrene-butadiene-rubber system binder, it cuts it in predetermined magnitude. A separator is microporous film made from polyethylene. Moreover, what dissolved LiPF₆ [1.5 mols / l] in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and ethyl methyl carbonate 1. was used for the organic electrolytic solution. The produced cylindrical cell is 650mm in the diameter of 18mm, and height. In addition, LiCO₂ was used as a positive pole active material for the comparison, and the cylinder cell was produced by the same approach. The result of having compared the electrical property of these cells was shown in Table 2.

[0057] After charging these cells by 100mA constant current until it was first set to 4.2V, the charge and discharge which discharge until it is set to 2.0V by 100mA constant current were performed. Capacity was checked for this charge and discharge in the number cycle repeat and the place where cell capacity became fixed mostly. The conditions of a check of capacity are as follows. Maximum current set charge to 1A by the constant-potential charge of 4.2V first. Termination of charge was considered as the time of a current value amounting to 50mA. Discharge discharged to 2.5V by 300mA constant-current discharge. Discharge capacity obtained at this time was made into the discharge capacity of a cell. The ambient atmosphere of charge and discharge was performed at 25 degrees C. Moreover, a high rate discharge ratio measures each discharge capacity with the current value (0.2C) of the rate discharge of 5 time amount, and the current value (2C) of the rate discharge of 0.5 time amount, when cell capacity is set to 1C, and it expresses it with the rate of a capacity factor of 2C [0 and]/2C. The rate of a discharge capacity factor at the time of discharging at the case where it discharges at 20 degrees C by 1C current, and -10 degrees C (-10 degrees C / 20 degrees C) showed the low-temperature discharge ratio. Moreover, the cycle life showed the rate of a capacity factor to the initial capacity in a 100 cycle time.

[0058]

[Table 2]

		容量 (mAh)	ハイレート 放電比率(%)	低温放電 比率(%)	サイクル 寿命
実施例 1	$\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$	1580	95	70	90
比較例 1	LiCoO_2	1500	92	50	85

[0059] The cell of this invention excels the result of Table 2 in all the examined items. Therefore, the cell which excelled LiCoO₂ which is the mainstream conventionally in applying to a lithium secondary battery by using the ingredient of this invention as positive active material can be offered.

[0060] The <<example 2 and example of comparison 2>> As mentioned above, the positive-electrode ingredient of this invention does so the effectiveness of suppressing expansion of a cell. In order to check this, the thin cell was produced, and thickness change of the cell accompanying charge and discharge, the rate of increased thickness of the cell accompanying a cycle, etc. were measured. The positive-electrode plate and the negative-electrode plate were produced by the approach shown in the example 1, and the same approach. However, the copolymer of 6 vinylidene fluoride [which can gel the electrolytic solution] (PVDF), and propylene fluoride (HFP) was used for the used binder to the usual binder, having added it. What applied to the fine porosity film of polyethylene PVDF-HFP which can gel this electrolytic solution also to a separator was used. Thus, the produced forward negative-electrode plate was wound through the separator, and it fabricated in the shape of flat on square shape cells, and considered as the group of electrode. Since a group of electrode and

a separator join to the posterior pole plates warmed at this time through a PVDF-HFP polymer by applying a pressure, such a process may be added. This group of electrode is inserted in the lamination bag of aluminum. The film of resin makes aluminium foil have rivaled, and resin can fuse and weld this bag by putting heat and a pressure.

[0061] The cell was obturated by carrying out heat welding of the lamination bag with the back vacuum into which the electrolytic solution was poured and liquid was infiltrated under vacuum next. The same thing as an example 1 was used also about the electrolytic solution. After obturation, by warming, the electrolytic solution swells in a polymer and it gels. The conditions of gelation are 80 degrees C - 90 degrees C, and are 1 - 3 hours. Moreover, by the initial charge, when there is much generation of gas, the process which removes this gas besides a system is put in. Some lamination bags of aluminum are enlarged, and resealing opening is carried out after extracting the gas which opens a bottom and occurs in an initial charge. Thus, the same approach as an example estimated the electrochemistry property of the produced cell. After capacity charged these cells until it is 50mA constant current and was first set to 4.2V, it performed the charge and discharge which discharge until it is set to 2.0V by 50mA constant current. Capacity was checked in the place where number cycle repeat **** cell capacity became fixed about this charge and discharge. The conditions of a check of capacity are as follows.

[0062] Maximum current set charge to 500mA by the constant-potential charge of 4.2V first. Termination of charge was considered as the time of a current value amounting to 20mA. Discharge discharged to 2.5V by 100mA constant-current discharge. Discharge capacity obtained at this time was made into the discharge capacity of a cell. The ambient atmosphere of charge and discharge was performed at 25 degrees C. Cell thickness measured the center section of the cell with slide calipers, and showed the difference of the thickness in a charge condition, and the thickness in a discharge condition. Moreover, the thickness change accompanying a cycle showed the difference of the thickness of the charge condition after 100 cycles, and the thickness of an initial charge condition similarly. Also in the thin cell which used LiCoO₂ as positive active material for the comparison, it was shown. The result of an experiment is shown in Table 3.

[0063]

[Table 3]

		容量 (mAh)	充放電に伴う 厚み変化 (mm)	サイクル後の 厚み変化 (mm)
実施例 2	$\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$	850	0.04	0.08
比較例 2	LiCoO_2	820	0.15	0.4

[0064] Change of cell thickness can be controlled by using the positive electrode of this example more clearly than Table 3.

[0065] <<example 3: -- reduction>> of polarization -- neither LiNiO₂ nor LiMnO₂ can say electronic conduction nature with it being so good. By this, especially at the time of a lifting and high rate discharge, capacity will decrease big polarization in the discharge last stage. A nickel element and a manganese element have the mutually different electronic structure. However, the electronic structure and the interaction of a different-species element which approached when these were dissolved on atomic level are caused. Especially in the combination of nickel and manganese, it acts so that this phenomenon may raise the electronic conduction nature of an ingredient, and the same conductivity as a metal can be given. This is considered that it can do clearly also by computational chemistry, such as a DV-x alpha process. As this also shows, it is important to form the solid solution in atomic level and that an adjoining atom is a heteroatom. When it puts in another way, the probability for the element with which dissolving by the ratio of 1:1 adjoins to be a different-species element will be the highest. This is the merit of mixing manganese with nickel by 1:1. As an example, in order to check this polarization phenomenon before $x=0.3-0.7$, it measured by the cell which shows the same trial as the high rate discharge rate measurement shown in Table 4 to drawing 18.

[0066]

[Table 4]

x	ハイレート放電率% (2 C / 0.2 C, 20℃)
0.3	71
0.4	92
0.5	95
0.6	91
0.7	65

[0067] Table 4 shows that a high rate discharge rate falls, when the value of x shifts from 0.5. Moreover, the rate is the limit where even about 10% can permit a fall, and if this is exceeded, it will fall rapidly. Furthermore, discharge potential also rises by about 100mV by mixing manganese with nickel. In LiNiO₂, in LiMnO₂, it is 3V in 4V. Usually, if it will predict from now on, it will be thought that in the case of nickel manganese you may be 3.5V since it is mixed by 1:1. However, when it is made to dissolve by 1:1, potential higher about 100 moremV than the discharge potential of LiNiO₂ is shown. This is also considered to be the proof to which the atoms of nickel and manganese are carrying out the interaction densely. This potential also had the highest time of x=0.5, and it turned out that it falls by from now on shifting.

[0068] <<example 4: -- stability>> of an ingredient -- if LiNiO₂ charges and Li falls out, it will become very unstable, it detaches oxygen at low temperature comparatively, and is returned to NiO. This is fatal when using it as positive active material of a cell, and it is expected that the oxygen to generate is led to the thermal run away of a cell, i.e., ignition and a burst, by the factor. This can also improve manganese by making it dissolve by the ratio of 1:1. The cell used in the example 3 was charged. then, a cell -- decomposing -- a positive electrode -- the mixture was taken out. This ingredient was covered over DSC (differential scanning calorimeter) measurement as it was. The exothermic peak observed at the lowest temperature acquired at this time is shown in Table 5.

[0069]

[Table 5]

x	DSC測定 of 1st ピーク温度 (℃)
0.3	180
0.4	220
0.5	228
0.6	222
0.7	190

[0070] Table 5 shows that the time of x=0.5 has the highest temperature. This shows that the time of x=0.5 is thermally [as an ingredient] stable. Moreover, it turns out that the gap from x=0.5 will become unstable rapidly thermally if 10% is the limit of permission and this is exceeded. In addition, although carbonaceous was used as an active material of a negative electrode in the example in order to evaluate the engine performance of a positive electrode, it is not limited to this and an alloy, a lithium metal, other oxides with comparatively low potential, a nitride, etc. can be adopted. Moreover, although what dissolved LiPF₆ [1.5 mols / l] in the mixed solvent of the volume ratio 1:1 of ethylene carbonate and ethyl methyl carbonate l. in the example was used also about the electrolytic solution, it is not limited to this and an organic or inorganic solid electrolyte etc. can be adopted.

[0071]

[Effect of the Invention] According to this invention, a cheap nickel manganese multiple oxide can be effectively used as positive active material, and a nonaqueous electrolyte cell with good charge-and-discharge effectiveness can be offered by high capacity.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram of the experiment facility used in order to manufacture positive active material with a coprecipitation method in this invention.

[Drawing 2] It is the SEM (scan type electron microscope) photograph of the front face of the positive-active-material particle produced in this invention.

[Drawing 3] It is the SEM photograph of the cross section of the positive-active-material particle produced in this invention.

[Drawing 4] It is the schematic diagram of another experiment facility used in order to manufacture positive active material with a coprecipitation method in this invention.

[Drawing 5] It is the SEM photograph of the positive-active-material particle produced in this invention.

[Drawing 6] It is the X diffraction image of the lithium content nickel manganic acid ghost obtained when it calcinated at each temperature.

[Drawing 7] It is the SEM photograph in which the particle shape of the lithium content nickel manganic acid ghost produced in this invention is shown.

[Drawing 8] It is the SEM photograph in which the particle shape of the lithium content nickel manganic acid ghost produced in this invention is shown.

[Drawing 9] It is drawing showing the X diffraction peak of the ingredient manufactured with the dry-blending calcinating method or the coprecipitation method.

[Drawing 10] It is drawing showing the X diffraction peak of the ingredient manufactured with the dry-blending calcinating method or the coprecipitation method.

[Drawing 11] It is drawing showing the charge-and-discharge curve of the coin mold cell which changes with the burning temperature of positive active material.

[Drawing 12] It is drawing showing the result of the X diffraction of positive active material.

[Drawing 13] It is drawing showing change of the lattice constant of positive active material.

[Drawing 14] It is drawing showing the volume change of the unit lattice calculated from a-axis Cho and c-axis Cho of positive active material.

[Drawing 15] It is drawing showing the discharge curve of LiCoO₂ (a) and LiNiO₂ (b).

[Drawing 16] It is drawing showing LiNi_{1/2}Mn_{1/2}O₂ (c), and the discharge curve of LiMnO₂ (d).

[Drawing 17] It is drawing showing LiNi_{1/2}Mn_{1/2} / discharge curve of 2O₂.

[Drawing 18] It is outline drawing of longitudinal section of the cylindrical cell produced in this example.

[Description of Notations]

1 Reaction Vessel

2 Tube

3 Rabble

4 Pump

5 Feed Hopper

6 Reaction Layer

7 Uptake Section

11 Cell Case

12 Obturation Plate

13 Insulating Packing

- 14 Group of Electrode
- 15 Positive-Electrode Lead
- 16 Negative-Electrode Lead
- 17 Insulating Ring

[Translation done.]

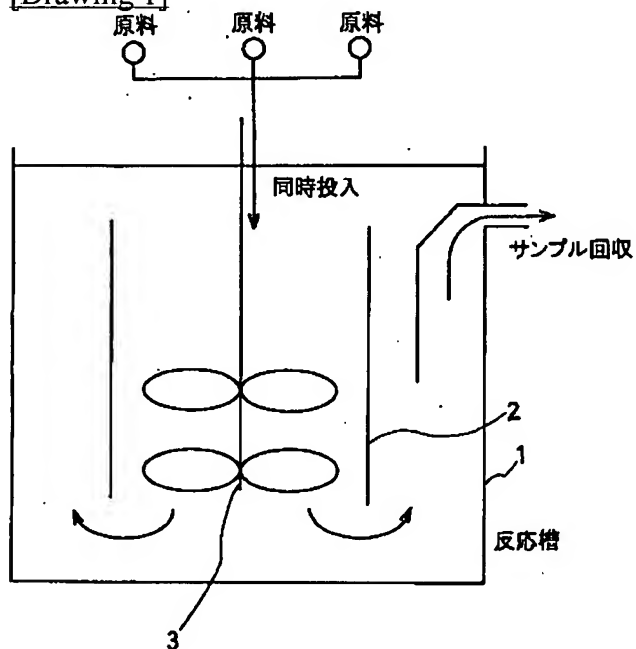
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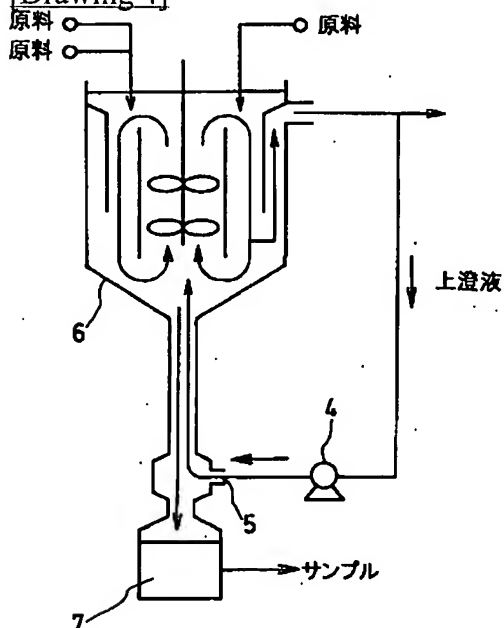
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DRAWINGS

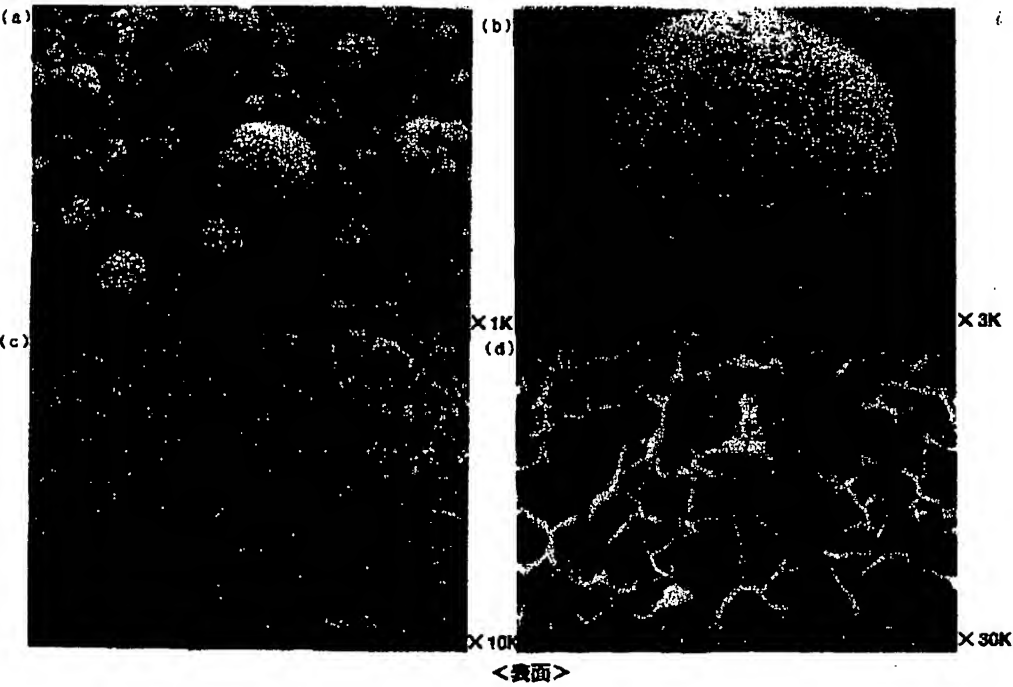
[Drawing 1]



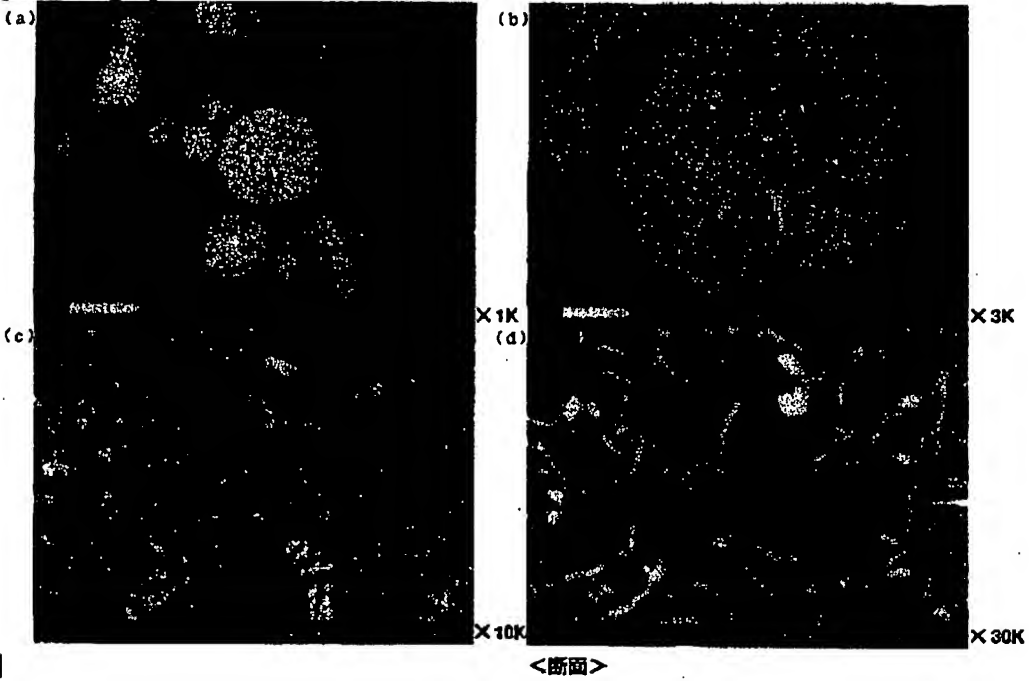
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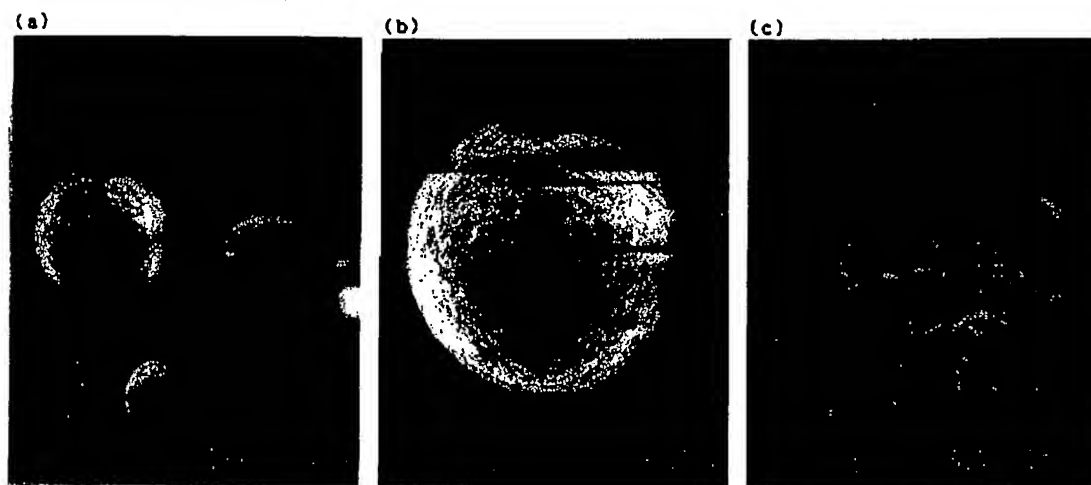
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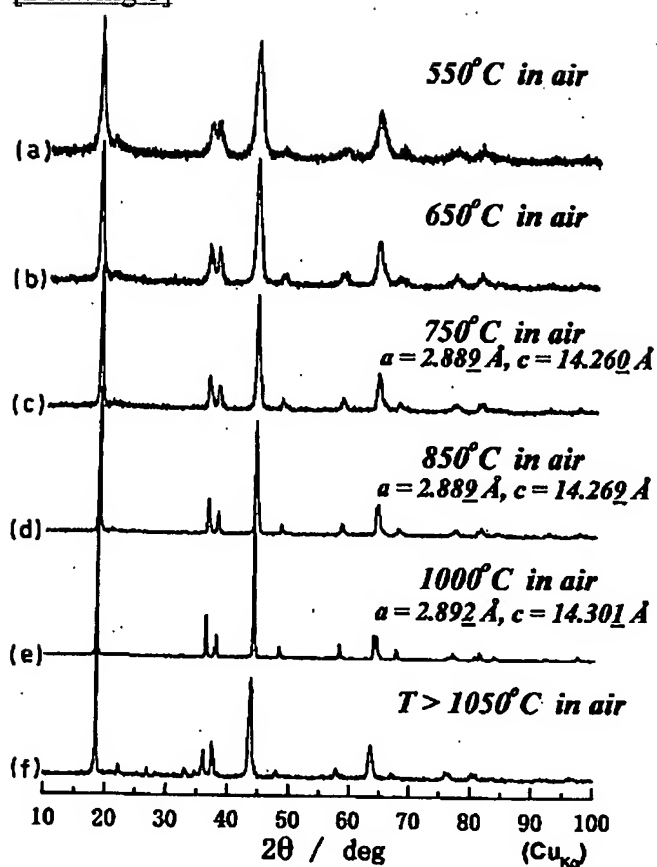
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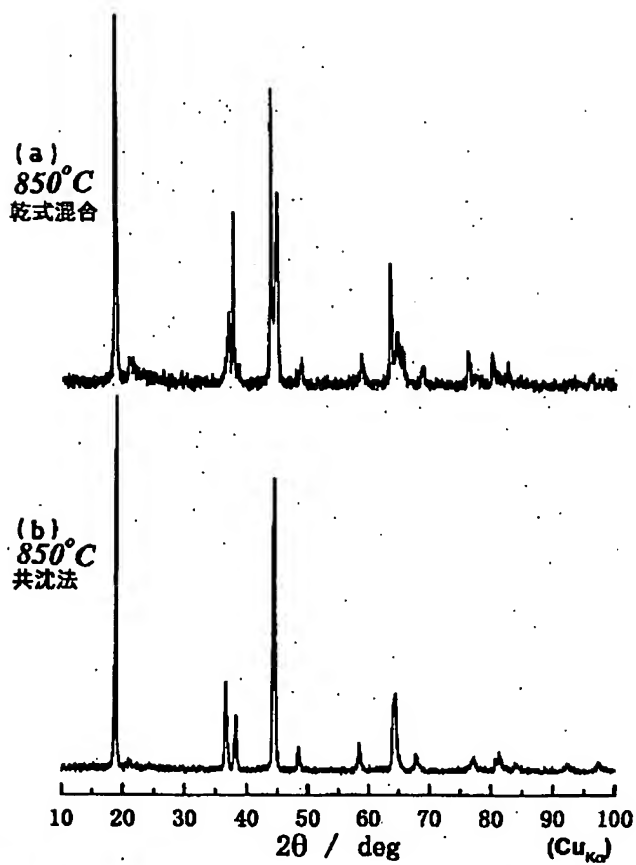
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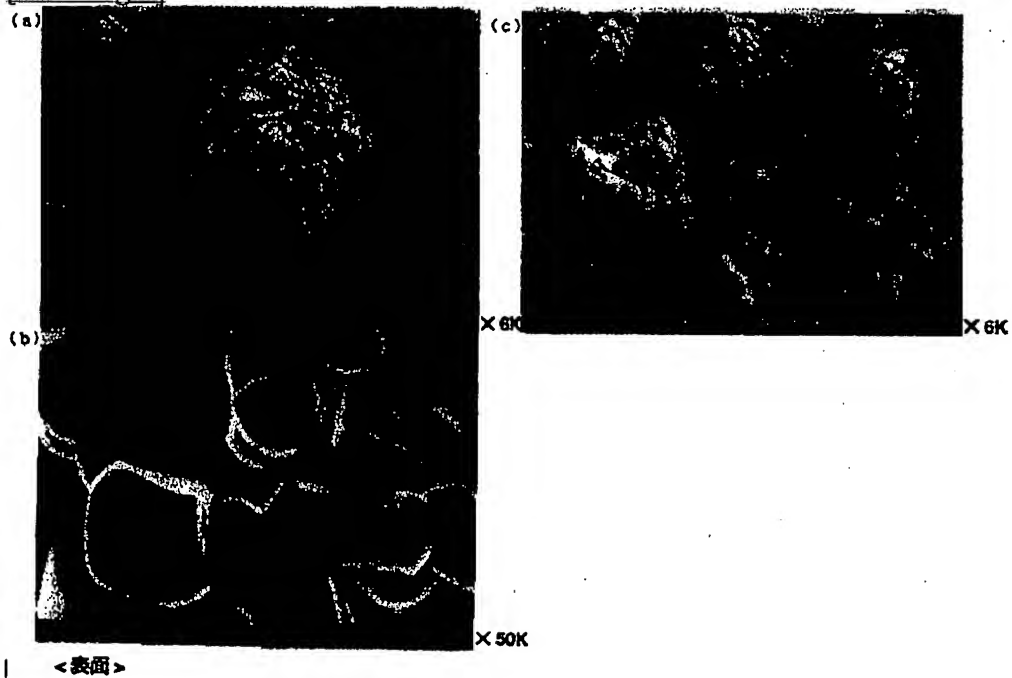
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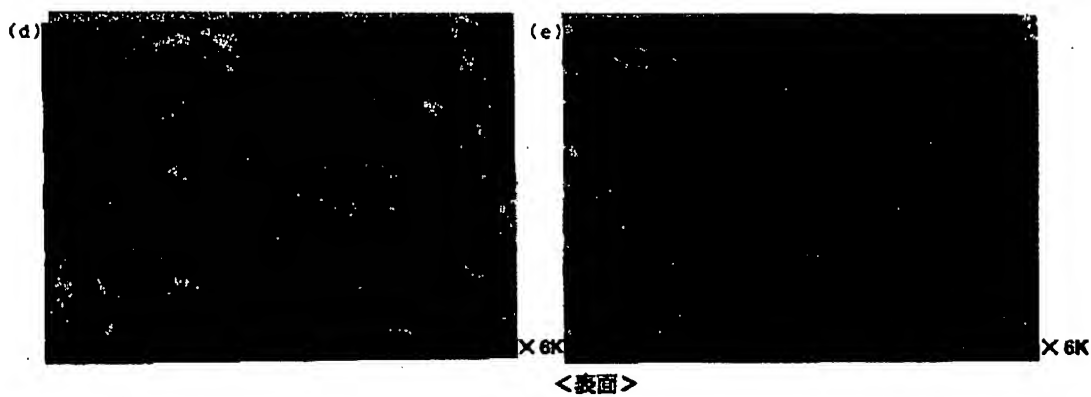
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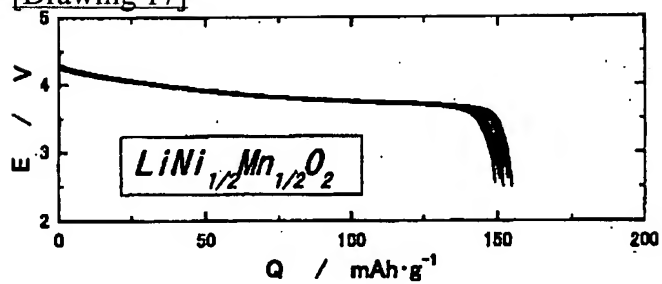
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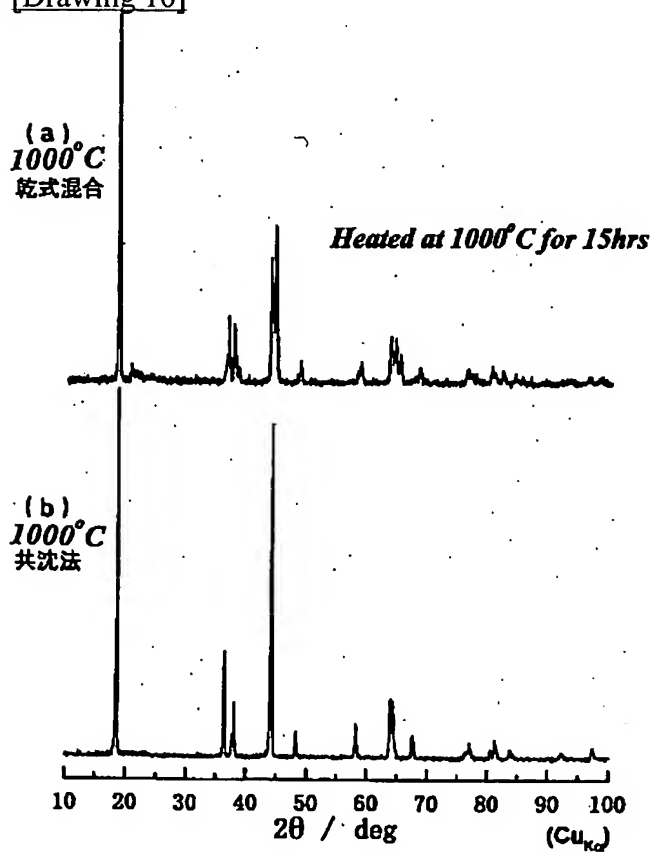
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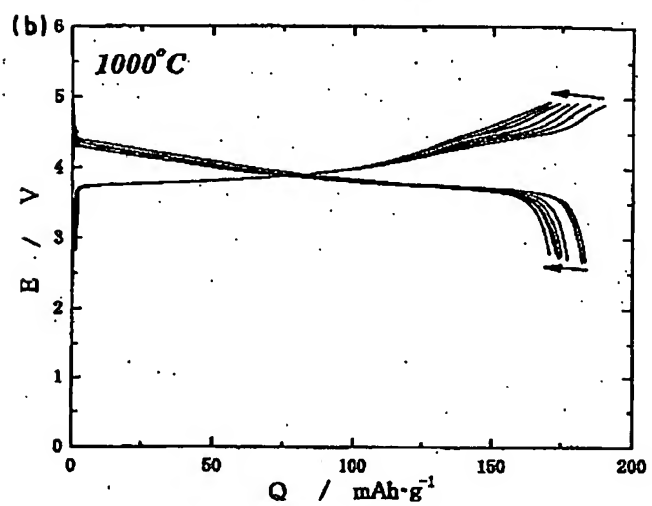
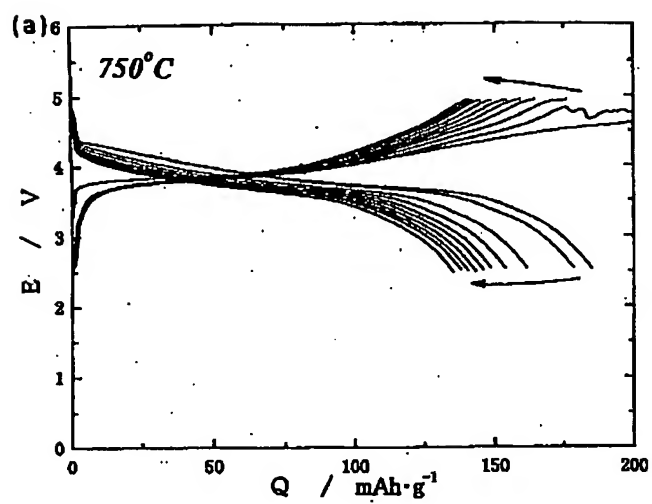
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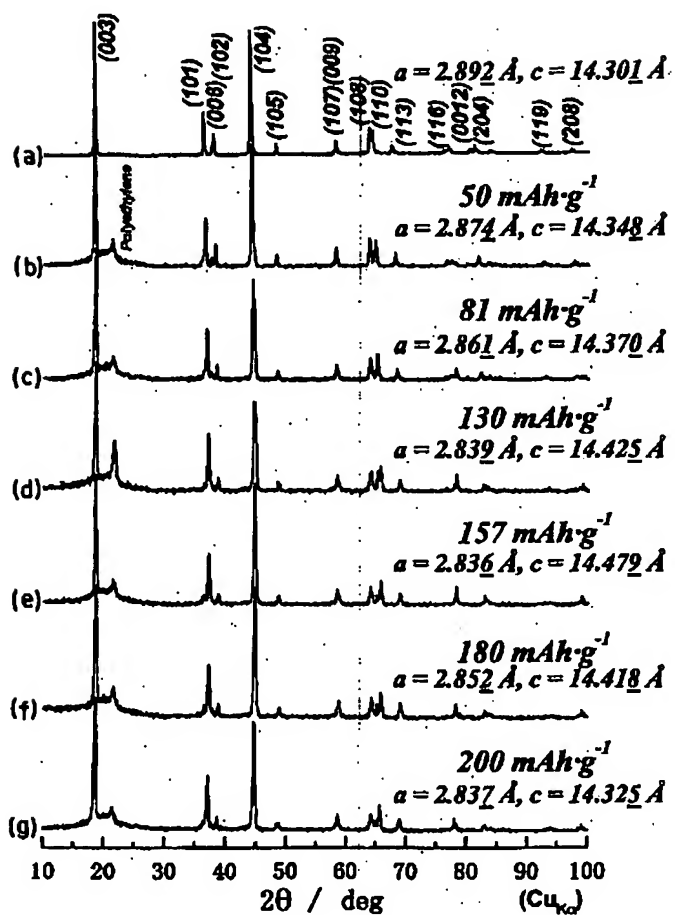
[Drawing 10]



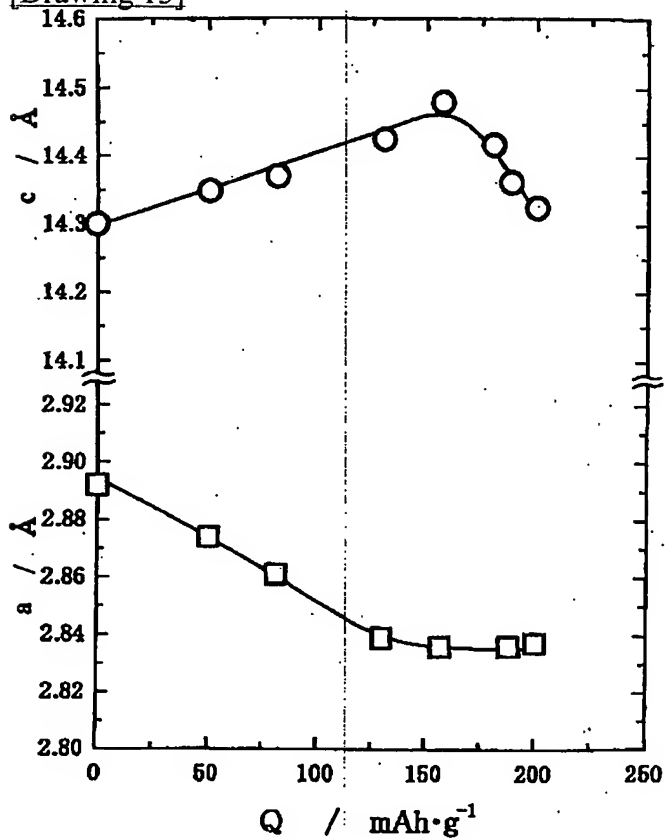
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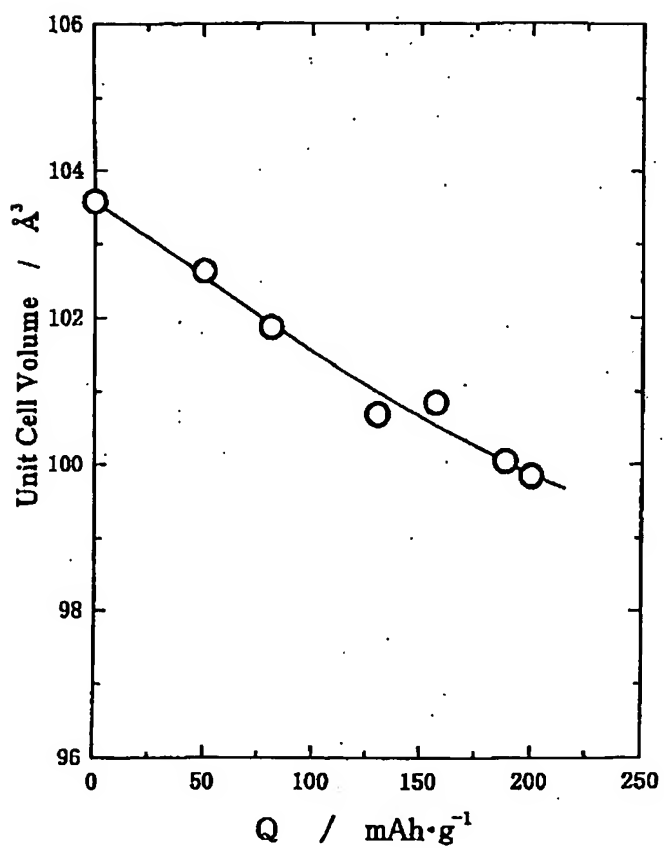
[Drawing 12]



[Drawing 13]

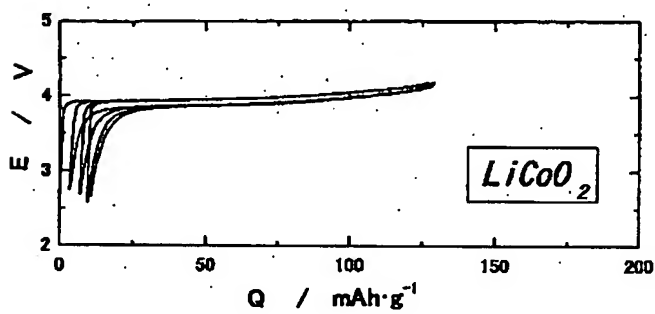


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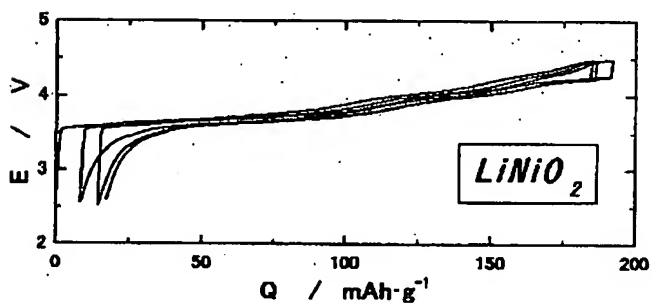


[Drawing 15]

(a)

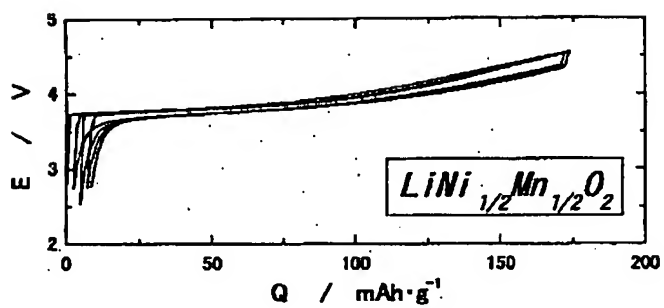


(b)

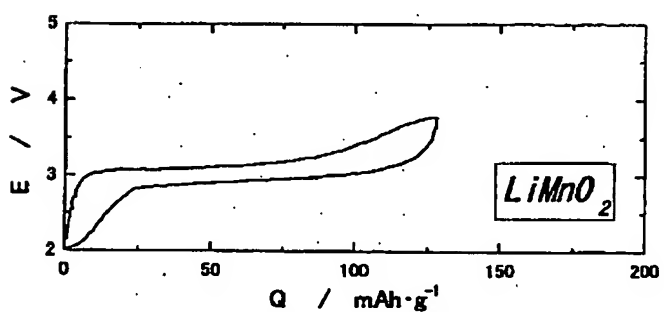


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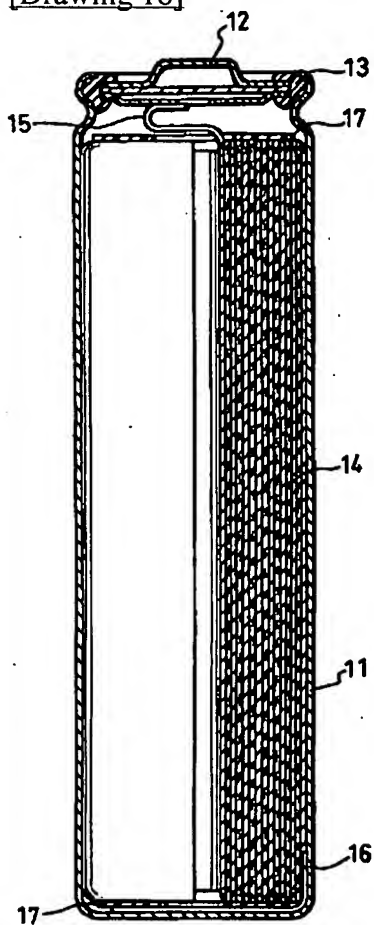
(c)



(d)



[Drawing 18]



[Translation done.]